

# APPLICATION OF INCIPIENT WET IMPREGNATION (IWI) METHODOLOGY IN THE SYNTHESIS OF Ni/SiO<sub>2</sub> CATALYSTS FOR HYDRODEOXYGENATION PROCESSES

AFOLABI O., ONWONA A.

University of Ghana, Department of Material Science and Engineering.

[hafeezafolabi@yahoo.com](mailto:hafeezafolabi@yahoo.com)

**Abstract** - The development of efficient catalysts is crucial for various industrial processes, including petrochemical production, hydrogenation reactions, and environmental remediation. Nickel-based catalysts have garnered significant attention due to their exceptional catalytic properties, cost-effectiveness, and wide applicability. In recent years, wet impregnation has emerged as a promising method for synthesizing nickel-based catalysts with enhanced performance and stability.

This abstract aims to provide a comprehensive overview of the inception of wet impregnation as a preferred technique for preparing nickel-based catalysts. It highlights the fundamental principles and mechanisms involved in the wet impregnation process, emphasizing the critical factors influencing catalyst performance, such as precursor selection, impregnation solvent, impregnation methods, and post-impregnation treatments.

Wet impregnation involves the deposition of catalytically active species onto a support material through the utilization of a liquid phase. The process begins with the selection of a suitable nickel precursor, which plays a pivotal role in determining the final catalyst properties. Various nickel salts, such as nickel nitrate, nickel acetate, or nickel chloride, have been employed as precursors, each offering unique advantages and challenges.

The choice of impregnation solvent is another crucial aspect that affects the catalyst's physicochemical properties. Solvents like water, alcohols, or organic acids are commonly used, and their selection depends on factors such as precursor solubility, stability, and environmental considerations.

Different impregnation methods, including incipient wetness impregnation, pore filling impregnation, and vacuum impregnation, have been explored to achieve uniform distribution of the active species on the support material. The impregnation process parameters, such as impregnation time, temperature, and pH, are carefully optimized to control the loading and dispersion of the active phase.

Post-impregnation treatments, such as drying, calcination, and reduction, significantly influence the final catalyst properties, including surface area, crystallinity, and metal-support interactions. The choice and optimization of these treatments are

critical to achieving desired catalytic performance and stability.

The inception of wet impregnation as a method for nickel-based catalyst synthesis has enabled the tailoring of catalyst properties, such as particle size, surface area, and metal dispersion, to meet specific reaction requirements. Additionally, the versatility of wet impregnation allows the incorporation of various promoters or modifiers, further enhancing the catalyst's activity and selectivity.

In conclusion, the inception of wet impregnation has revolutionized the synthesis of nickel-based catalysts, providing a flexible and efficient approach to engineer catalytic materials. By understanding the key factors influencing catalyst performance, this research exploits the potential of wet impregnation to design advanced nickel-based catalysts for diverse industrial applications.

**Keywords:** efficient catalysts, environment, industrial applications, wet impregnation

## 1. INTRODUCTION

Wet impregnation is a widely used technique in catalyst preparation, including the development of nickel-based catalysts. It involves the deposition of catalytically active species onto a solid support material through the use of a liquid solution or suspension.

Nickel-based catalysts are highly desirable in various industrial processes, such as hydrogenation, reforming, and ammonia synthesis. The wet impregnation method allows for precise control over the loading of active metal species onto the support material, leading to enhanced catalytic performance.

The process of wet impregnation typically begins with the selection of a suitable support material. Commonly used supports include metal oxides like alumina (Al<sub>2</sub>O<sub>3</sub>), silica (SiO<sub>2</sub>), and titania (TiO<sub>2</sub>). These supports provide a high surface area and mechanical stability to the catalyst.

The impregnation solution consists of a soluble nickel precursor, such as nickel nitrate or nickel chloride, dissolved in a suitable solvent. Other additives, such as stabilizers or promoters, may be included in the solution to enhance the catalytic properties or stability of the resulting catalyst.

The impregnation process involves immersing the support material in the impregnation solution, allowing the active metal species to diffuse into the porous structure of the support. The impregnation can be performed by either incipient wetness impregnation or conventional wet impregnation.

In the case of incipient wetness impregnation, the support material is saturated with the impregnation solution without leaving any excess liquid. This ensures that the active metal species are loaded as uniformly as possible onto the support, maximizing the dispersion and minimizing the formation of metal clusters.

After impregnation, the catalyst precursor-loaded support is dried to remove the solvent, typically by heating at moderate temperatures. Subsequently, the dried catalyst precursor is subjected to a calcination or reduction step, where it is heated under controlled conditions to convert the precursor into the desired active metal state, such as metallic nickel.

The final catalyst obtained through wet impregnation exhibits high activity due to the uniform dispersion of the active metal species on the support material. The catalyst's performance can be further optimized through various post-impregnation treatments, such as reduction, sulfidation, or surface modification.

In summary, wet impregnation is a versatile and effective method for preparing nickel-based catalysts. The incipient wetness impregnation variant ensures uniform loading of the active metal species onto the support, leading to improved catalytic performance in various industrial applications.

## 2. OBJECTIVES

The incipient wet impregnation (IWI) method is commonly used in catalyst preparation, including Nickel-based catalysts. The primary objectives of employing the IWI technique for Nickel-based catalysts are as follows:

### 2.1. Active metal dispersion

The IWI method aims to achieve a high dispersion of the active metal, in this case, Nickel, on the catalyst support. The goal is to distribute the Nickel species evenly across the support surface, leading to increased accessibility of the active sites during catalytic reactions.

### 2.2. High loading efficiency

IWI allows for a controlled and precise deposition of the active metal onto the catalyst support. This method aims to achieve high loading efficiency, meaning that a significant amount of the Nickel precursor is successfully incorporated onto the support without excessive loss during the impregnation process.

### 2.3. Catalyst stability

Another objective of IWI is to enhance the stability and durability of the catalyst. By depositing Nickel species uniformly onto the support, the IWI method helps to prevent the agglomeration or sintering of the active

metal particles during catalytic reactions, thereby maintaining the catalytic activity and extending the catalyst's lifespan.

### 2.4. Controllable catalyst properties

IWI offers control over various catalyst properties such as metal loading, particle size, and distribution. By adjusting the impregnation parameters, such as precursor concentration, impregnation time, and drying conditions, it is possible to tailor the catalyst properties to meet specific performance requirements.

### 2.5. Improved catalytic activity and selectivity

The primary objective of catalyst preparation, including IWI, is to enhance the catalytic activity and selectivity of the Nickel-based catalyst. By achieving a high dispersion of Nickel species, controlling the catalyst properties, and optimizing the metal-support interaction, the IWI method can contribute to improved catalytic performance, enabling desired reactions with high conversion rates and selectivity.

Overall, the objectives of employing the incipient wet impregnation method for Nickel-based catalysts revolve around achieving high active metal dispersion, loading efficiency, catalyst stability, and controllable properties to enhance catalytic activity and selectivity.

## 3. METHODOLOGY

The incipient wet impregnation method is a common technique used to prepare supported catalysts, including nickel-based catalysts. This method involves the deposition of a metal precursor onto a support material, followed by subsequent reduction or activation steps to convert the precursor into the active catalytic species. Here is a general methodology for the incipient wet impregnation of nickel-based catalysts:

### 3.1. Support material selection

Choose a suitable support material based on the specific requirements of your catalytic application. Common support materials include alumina, silica, zeolites, and carbon.

### 3.2. Pretreatment of the support material

Prior to impregnation, it is important to pretreat the support material to remove any impurities or surface contaminants. This typically involves calcination or activation at elevated temperatures to enhance the surface area and remove moisture.

### 3.3. Preparation of the metal precursor solution

Dissolve a suitable nickel precursor, such as nickel nitrate or nickel chloride, in a solvent. The choice of solvent depends on the solubility of the precursor and compatibility with the support material. Common solvents

include water, ethanol, or a mixture of water and organic solvents.

### 3.4. Impregnation process

Add the calculated amount of the metal precursor solution to the support material while maintaining agitation or stirring to ensure uniform distribution. The volume of the precursor solution is determined based on the desired metal loading on the catalyst.

### 3.5. Incipient wetness

The term "incipient wetness" refers to the addition of just enough precursor solution to saturate the support material's pores without excess liquid. This helps to maximize the metal dispersion and minimize agglomeration.

### 3.6. Drying

After the impregnation step, remove the excess solvent by drying the impregnated material. This can be done by placing the impregnated support in an oven or using other drying techniques, such as freeze-drying or vacuum drying.

### 3.7. Reduction/Activation

To convert the metal precursor into the active catalyst, a reduction or activation step is typically performed. For nickel-based catalysts, reduction with hydrogen (H<sub>2</sub>) is commonly employed. The reduction step is carried out at elevated temperatures (e.g., 300-500°C) in a hydrogen atmosphere.

### 3.8. Post-treatment (optional)

Depending on the specific catalyst requirements, additional post-treatment steps may be necessary. These can include calcination, sulfidation, or other treatments to further enhance the catalyst's activity, selectivity, or stability.

It's important to note that the exact details of the methodology may vary depending on the specific catalyst system and desired properties. Therefore, it is recommended to consult relevant literature, scientific articles, or expert guidance when performing the incipient wet impregnation of nickel-based catalysts to optimize the process for your specific needs.

## 4. EXPERIMENTAL APPROACH

Ni/SiO<sub>2</sub> catalyst was prepared using the Incipient Wet Impregnation method (IWI) with NiO<sub>2</sub> as the precursor and SiO<sub>2</sub> as the support. SiO<sub>2</sub> was procured from the commercial market. Before its application, SiO<sub>2</sub> was added to CHCl<sub>3</sub> solution and stirred for 2 hours. washed until filtrate attained neutrality. SiO<sub>2</sub> was recovered through centrifugation and dried overnight. NiO<sub>2</sub> was subjected to the same process. Recovered SiO<sub>2</sub> support and NiO<sub>2</sub> precursor were reintroduced into a stirring CHCl<sub>3</sub>

solution targeting a precursor loading of 5wt% and stirred for 1hr. Ni/SiO<sub>2</sub> was recovered through centrifugation and dried in a vacuum overnight. Recovered Ni/SiO<sub>2</sub> was designated sample 1. Another sample prepared was calcinated at 350°C in a batch reactor. Both samples were subjected to characterization using XRD and FT-IR. The figure 1 illustrates the process of IWI. (Incipient Wet Impregnation Method).

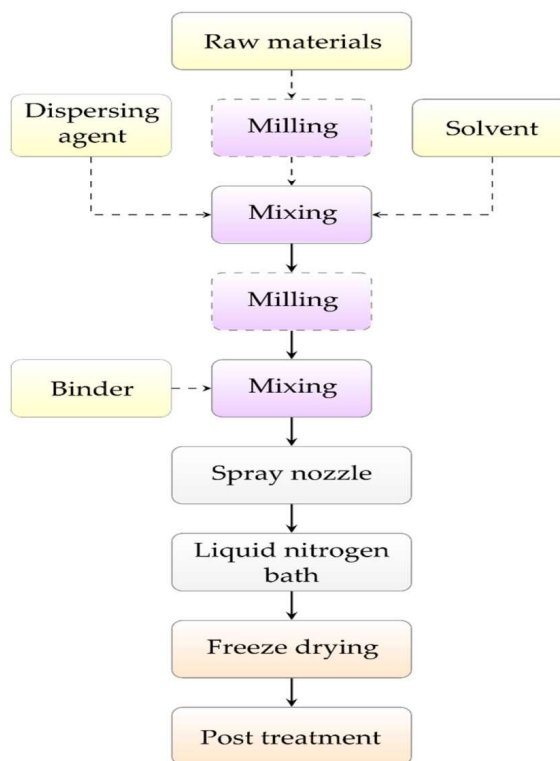


Fig. 1. Flowchart describing all stages of the incipient wet impregnation method of catalyst synthesis.

## 5. CHARACTERIZATION OF CATALYST

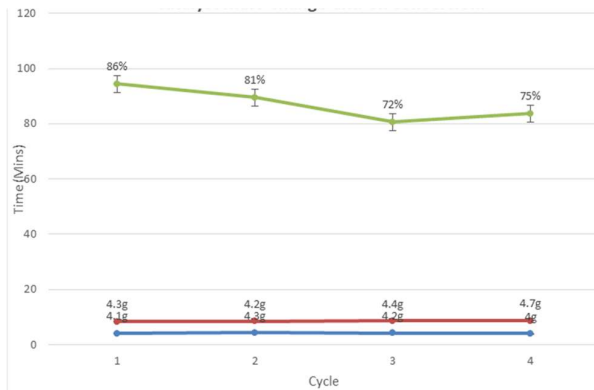
### 5.1. Stability and Re-usability Test

The stability and re-usability Ni/SiO<sub>2</sub> catalyst was determined in the production of biodiesel from waste oil to confirm the sustainability of the catalysts. Reaction was carried out in a batch reactor at 300°C and atmospheric pressure. For every sample recovered, resultant mixture was filtered to retrieve residual catalyst. Catalyst was dried and inspected for any mass gain due to carbon deposition or mass loss due to scintering or deactivation. The procedure was repeated four times. Note that catalyst was used after extraction from mixture after every cycle. Catalyst used for the first three runs displayed immense stability. 1, 2 and 3 denote catalytic runs, while value of oil conversion was defined in %. Oil conversion maintained a range of 72% to 86% from the 1st run to the 3rd run over 60mins, displaying catalyst efficacy. A marginal increase was recorded in the 4th run after a drop in oil conversion in the 3rd cycle to 72%, this could be a momentary build up of carbon on the catalyst surface of impurities within the system. The increase in the 4th cycle

points at the latter. Catalyst displayed stability with minimal mass loss in catalyst over the four cycles also evident in the high percentage of oil conversion over 4 runs.

**Table 1. Illustrating relationship between time, catalyst mass change and oil conversion**

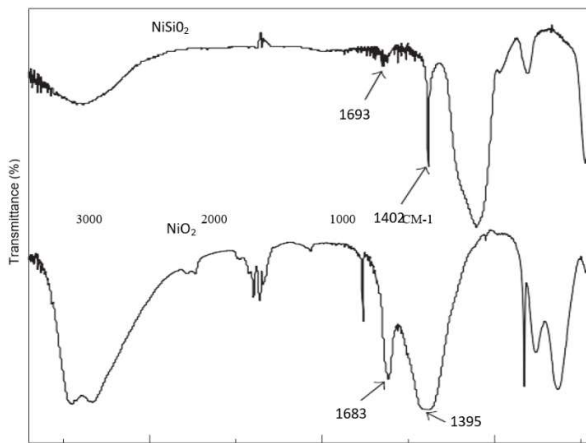
| Cycle | Time (MINS). | Initial Mass (G). | Final Mass (G). | Oil Conversion (%) |
|-------|--------------|-------------------|-----------------|--------------------|
| 1     | 15           | 4.1               | 4.3             | 86                 |
| 2     | 30           | 4.3               | 4.2             | 81                 |
| 3     | 60           | 4.2               | 4.4             | 72                 |
| 4     | 90           | 4.0               | 4.7             | 75                 |



**Fig. 2. Graph showing relationship between process time, mass change and oil conversion**

**5.2. FT-IR**

FT-IR spectra was measured using a spectrometer equipped with an MCT deflector . Pattern recovered from spectra is displayed in fig 3 below. NiO<sub>2</sub> and Ni/SiO<sub>2</sub> samples were subjected to FT-IR and investigated over a wavelength of 1000CM<sup>-1</sup> to 3000CM<sup>-1</sup>. FT-IR images revealed a symmetric shift in NiO<sub>2</sub> before and after impregnation on SiO<sub>2</sub>. Symmetric peaks are indicated by arrows on the image.

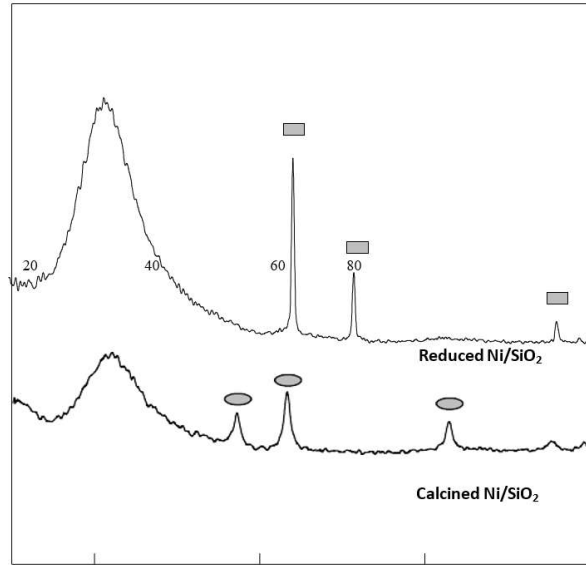


**Fig. 3. FT-IR analysis of NiO<sub>2</sub> and Ni/SiO<sub>2</sub>**

**5.3. XRD ANALYSIS**

X-Ray powder diffraction patterns of Ni/SiO<sub>2</sub> catalysts were obtained with an automated powder X-Ray

diffractometer equipped with a computer for data acquisition and analysis. Original samples were used directly after calcination in air for 2hrs at 400°C. A second set of samples were reduced by passing H<sub>2</sub> at 60L/min-1 for 2hrs at 400°C prior to XRD analysis and cooled to room temperature in a hydrogen atmosphere. All the particles were grinded to fine powder in an agate mortar before XRD analysis. The Figure 4 was obtained after the analysis.



**Fig. 4. XRD patterns of Ni/SiO<sub>2</sub> before and after reduction in H<sub>2</sub> for 1 h**

**6. RESULTS AND DISCUSSION**

The synergy between precursor and support in the Ni/SiO<sub>2</sub> catalyst synthesized for the catalytic hydrodeoxygenation of biodiesel was evident as shown in Fig.6.1 and 6.7.1 . A range of oil conversion from (72-86)% is an indication of the suitability of Ni/SiO<sub>2</sub> catalyst for the process. FT-IR spectra of Ni/SiO<sub>2</sub> before calcination was illustrated in Fig- above. Centering of bands of NiO<sub>2</sub> at 1683CM<sup>-1</sup> and 1385CM<sup>-1</sup> were synonymous with asymmetric and symmetric vibrations of Nitrate. After impregnation of NiO<sub>2</sub> on SiO<sub>2</sub> support, a cluster wavelength was indicated by the two bonds 1693CM<sup>-1</sup> and 1402CM<sup>-1</sup> respectively. This shift is as a result of the interaction between the precursor and the support. Both patterns are represented by the patterns in the fig 6.6.1 above.

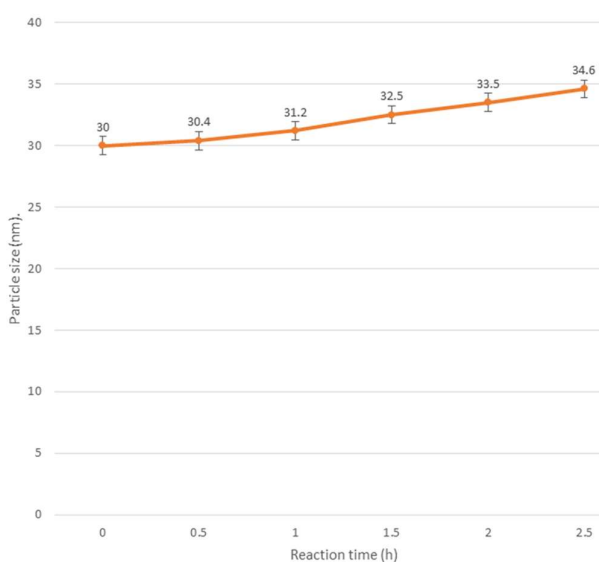
**6.1. XRD Analysis**

The crystalline structure of Ni/SO<sub>2</sub> catalyst was investigated using XRD. Fig- represents the results. The XRD patterns of all samples exhibited broad peak around 24o largely due to the presence of the SiO<sub>2</sub> support. After calcination, the sample showed only the FCC-NiO phase with typical reflections of the (111) (200) (220) planes at 39° 45° and 67°. The peaks assigned to NiO disappeared after reduction in H<sub>2</sub> for 3hours. 3 other peaks were visible around 44o 55o 76o for Ni(111), Ni(200) and Ni

(220) planes. This indicates the transformation of NiO to metallic Ni after H<sub>2</sub> reduction.

## 6.2. Effects of Particle size of Ni Precursor

The catalytic performance of Ni based catalysts is widely accepted and influenced by the crystalline size of metallic Nickel. Smaller Nickel particles provide more active sites for reactions to take place. Investigating the dependence of particle size on catalytic performance and efficiency Ni/SiO<sub>2</sub> catalysts after 4 different time were taken and estimated with XRD. For all samples only Ni and amorphous SiO<sub>2</sub> phases were detected by XRD, no NiO<sub>2</sub> phase was found meaning no significant change in the Ni phase was found. Diffraction intensity of Nickel increased over reaction time. The crystalline size of Nickel in Ni/SiO<sub>2</sub> catalyst as a function of reaction time was shown in fig 5 below.



**Fig. 5. Graph showing effects of reaction time on particle size**

The 30.0nm, 30.4nm, 31.2nm, 32.5nm, 33.5nm and 34.6 after 0, 0.5h, 1.0h, 1.5h, 2.0h and 2.5h reaction time. The change in crystalline size was an indication of the catalytic activity of Ni/SiO<sub>2</sub>. Comprehensively, the characterization results, carbon was not detected on the spent catalyst suggesting no carbon deposition during the reaction, the only peak detected was that of the Ni, no other species such as NiO<sub>2</sub> was detected, this concluded that the alteration and transformation of the Ni didn't cause any deactivation of Ni/SiO<sub>2</sub>. The potent interaction displayed between Ni and SiO<sub>2</sub> is a reason for the catalysts resistance to deactivation during the hydrodeoxygenation process.

## 7. CONCLUSION

Conclusively, Ni/SiO<sub>2</sub> catalysts was prepared by (IWI) method for the the hydrodeoxygenation of biodiesel and characterized by X-Ray diffraction and FT-IR. Ni/SiO<sub>2</sub> was calcined at 350°C, cooled and reduced to metallic Ni

by H<sub>2</sub> reduction at the same temperature. Active Nickel particles of Ni/SiO<sub>2</sub> were dispersed properly and positively interacted with SiO<sub>2</sub>, Scintering was non existent as a result of the positive interaction between precursor. SiO<sub>2</sub> greatly reduced the probability of Ni particle migration due to its larger specific surface area and pores, hence the sustainability and suitability of the catalyst was established.

## REFERENCES

- [1]. Combustion efficiency, impact of biofuels. A Demirbas pages 602-609, 02 Mar 2009.
- [2]. The analysis of the combustion behaviour of ethanol, butanol, iso octane, gasoline and methane in a direct injection spark ignition research engine. J. Serras Pereira, P.G Aleiferis, D. Richardson. Pages 484-513, July 2012.
- [3]. ACS, Sustainable Chemistry and Engineering, High throughout continous synthesis of Nickel Nano particles for the catalytic hydrogenation of Guaiacol. Emily J. Roberts, Susan E. Habas, Lu Wang, Daniel A. Ruddy. 2017.
- [4]. Combustion efficiency, impact of biofuels. A Demirbas pages 602-609, 02 Mar 2009.
- [5]. The analysis of the combustion behaviour of ethanol, butanol, iso octane, gasoline and methane in a direct injection spark ignition research engine. J. Serras Pereira, P.G Aleiferis, D. Richardson. Pages 484-513, July 2012.
- [6]. Overview on catalytic deoxygenation for biofuel synthesis using metal oxide supported catalysts. Xian Yih Ooi, Keat Teong Lee. 2013.
- [7]. Catalytic deoxygenation of oil and biodiesel of licuri to obtain n-alkanes with chains in the range of biojet fuels. Pedro H.M. Araujo, Ary. S. Maia, Angela M.T.M. Cordeiro, Amanda D. Gondim and Nataly A. Santos. 2014.
- [8]. Development and characterization of heterogeneous kaolin/ash based catalyst system, Edeh Friday, J.m Joel, Jibrin M Yelwa, J.M Joel, Jeffery Barminas. Dec 2018.
- [9]. Synthetic methods 1- chiral pool and diastereoselective methods. comprehensive Chirality Y Guindon. 2012.
- [10]. Synthetic methods iii-catalytic Methods C-C bond formation. S.Koboyashi, Y. Yamashida (2012).
- [11]. Hydrotreating lipids for aviation biofuels derived from extraction of wet and dry algae by Ze Shi Bing, Wei Zhao Shun. 2020.
- [12]. Direct hydrogenation of amides to alcohols and amines under mild conditions. Ekambaram Balaraman, Boopathy Gnanapra Kajam, Linda J. W Shimon, David Milstein. Nov 4 2010.
- [13]. Hydrogenation for biofuel production. Prof. Derek Creaser, Hu Chaoquan.
- [14]. Overview on catalytic deoxygenation of biofuel synthesis using metal oxide supported catalysts. Xian I Loo, Chyun Onju, Ching Juan Wei. 2011.
- [15]. Upgrading of bio fuels by the catalytic deoxygenation of biodiesel, Korean Journal of Chemical Engineering, Vol 29. Chong Hyun Ko, Sung Hoon Park, Jong Ki Jean, Kwang Eun Jeong. 2007.
- [16]. Selective deoxygenation of bio mass derived bio-oils within hydrogen modest environment. Kyle. A Rogers, Prof Ying Zheng. 2013.
- [17]. Deoxygenation of triolein to green diesel in an H<sub>2</sub> free condition: Effects of transition metal oxide supported on Zeolite. Choo Min Yee, O Lee Ing, Linh Tao Chuan, Lin Yo Chuan. 2021.

- [18]. Alternate energy sources, green chemistry and engineering, Mukesh Doble, Anil 2007.
- [19]. Prospects of biodiesel feedstock as an effective ecofuel source and their challenges, Advances in ecofuels for a sustainable environment , E.F Aransiola, B.O Solomon. 2019.
- [20]. Application of transesterification technologies, bioenergy with carbon capture and storage (BECCS), Clean energy for sustainable development, M.A Quander, S.Ahmed. 2017.
- [21]. Advances in bio-oil extraction from non edible seeds and algae biomass, advances in eco fuels for sustainable environment G.Basker, I Abumaebenezer, Selva Kumari. 2018
- [22]. Lignocellulose based chemical products, bioenergy research, advances and applications. E.D de Jung, Richard j.A Gosselink. 2014.
- [23]. Heterogeneous and homogeneous for petroleum catalysis, Wayne P.Schamuel, Anja Rumplecker, Joel M. Cizron, Eric C. Scher, Fabio Zuricher. 2012.
- [24]. 13<sup>th</sup> International symposium of process systems engineering (PSE) 2010. Hye Ji Lee, Jin Min Lee, Computer Aided Chemical Engineering. 2018.
- [25]. Ingeniería de Las reacciones Químicas. Tipo de reactores, chemical process engineering Design. By Harry Silla. 2018.
- [26]. Demirbas A. Progress and recent trends in biofuels. Prog Energy Combust Sci 2007;33:1–18.
- [27]. Keskin A, Guru M, Altiparmak D, Aydin K. Using of cotton oil soapstock biodiesel–diesel fuel blends as an alternative diesel fuel. Renew Energy 2008;33:553–557. 2018.
- [28]. Canakci M, Van Gerpen J. Biodiesel production from oils and fats with high free fatty acids. Trans ASAE 2001;44:1429–36. 2016.
- [29]. Papadopoulos CE, Lazaridou A, Koutsoumba A, Kokkinos N, Christoforidis A, Nikolaou N. Optimization of cotton seed biodiesel quality (critical properties) through modification of its fame composition by highly selective homogeneous hydrogenation. Biores Technol 2010;101:1812–1819.
- [30]. Srivastava A, Prasad R. Triglycerides-Based Diesel Fuels. Renew Sust Energy Rev 2000;4:111–133. 2018.
- [31]. Rao P, Gopalakrishnan K. Vegetable Oils and Their Methyl esters as Fuels for Diesel Engines. Indian J Technol 1991;29:292–29. 2014.
- [32]. Aksoy F, Bayrakceken H, Eryilmaz T, Aksoy L. Analyzing the impact of using different methyl esters in a diesel engine on engine performance and emissions. Energy Educ Sci Technol Part A 2011;27:25–34. 2016.
- [33]. Aksoy F. The effects of sunflower oil and soybean oil – diesel fuel blends on engine performance and emissions. Energy Educ Sci Technol Part A 2011;27:419–426. 2015.
- [34]. Aksoy F, Bayrakceken H, Baydır SA, Yavuz H. The effects on the engine performance and emission of pre-heating application in the canola oil methyl ester. Electronic J Vehicle Technol 2009;1:25–33 [in Turkish]. 2012.
- [35]. Altun S. Fuel properties of biodiesels produced from different feedstocks. Energy Educ Sci Technol Part A 2011;26:165–174. 2011.
- [36]. Fukuda H, Kondo A, Noda H. Biodiesel Fuel Production by Transesterification of Oils. J Biosci Bioeng 2001;92:405–416. 2013.
- [37]. Tyson K, S. Biodiesel Handling and Use Guidelines, Report of National Renewable Energy Laboratory, NREL/TP-580-3004, USA, 1–3, 2001.
- [38]. Van Gerpen J. Biodiesel processing and production, Fuel Procg Technol 2005;86:1097–1107. 20119.
- [39]. Cetinkaya M, Ulusoy Y, Tekin Y, Karaosmanoglu F. Engine and winter road test performances of used cooking oil originated biodiesel. Energy Convers Manage 2005;46:1279–1291.
- [40]. Arkoudeas P, Kalligeros S, Zannikos G, Anastopoulos G, Karonis D, Korres D. Lois,E. Study of using JP-8 aviation fuel and biodiesel in CI engines. Energy Convers Manage 2002;44:1013–1025.
- [41]. Altin R, Cetinkaya S, Yucsu HS. The potential of using vegetable oil fuels as fuel for diesel engines. Energy Convers Manage 2001;42:529–38.
- [42]. Dorado MP, Ballesteros E, Arnal JM, Gomez J, Gimenez Lopez FJ. Exhaust emissions from a diesel engine fueled with transesterified waste olive oil. Fuel 2003;82:1311–1315.
- [43]. Nwafor OMI. Emission characteristics of diesel engine operating on rapeseed methyl ester. Renew Energy 2004;29:119–129.
- [44]. Usta N. An experimental study on performance and exhaust emissions of a diesel engine fuelled with tobacco seed oil methyl ester. Energy Convers Manage 2005;46:2373–2386.
- [45]. Monyem A, Van Gerpen JH. The effect of biodiesel oxidation on engine performance and emissions. Biomass Bioenergy 2001;20:317–32.
- [46]. Usta N, Ozturk E, Can O, Conkur ES, Nas S, Con AH, Can AC, Topcu M. Combustion of biodiesel fuel produced from hazelnut soapstock/waste sunflower oil mixture in a diesel engine. Energy Convers Manage 2005;46:741–755.
- [47]. Scholl KW, Sorenson SC. Combustion of Soybean Oil Methyl Ester in a Direct Injection Diesel Engine, SAE Paper, No.930934, 1999.
- [48]. Development of Stable Oxygen Carrier Materials for Chemical Looping Processes—A Review, Yoran De Vos, Marijke Jacobs, Pascal Van De Vort July 2020.
- [49]. Hydrogenation for biofuel production. Prof. Derek Creaser, Hu Chaoquan. 2012.
- [50]. Development and characterization of heterogeneous kaolin/ash based catalyst system, Edeh Friday, J.m Joel, Jibrin M Yelwa, J.M Joel, Jeffery Barminas. Dec 2018.
- [51]. Synthetic methods 1- chiral pool and diastereoselective methods. comprehensive Chirality Y Guindon. 2012.
- [52]. Synthetic methods iii-catalytic Methods C-C bond formation. S.Koboyashi, Y. Yamashida (2012).
- [53]. Hydrotreating lipids for aviation biofuels derived from extraction of wet and dry algae by Ze Shi Bing, Wei Zhao Shun. 2002.
- [54]. Direct hydrogenation of amides to alcohols and amines under mild conditions. Ekambaram Balaraman, Boopathy Gnanapra Kajam, Linda J. W Shimon, David Milstein. Nov 4 2010.
- [55]. Hydrogenation for biofuel production. Prof. Derek Creaser, Hu Chaoquan. 2019.
- [56]. Overview on catalytic deoxygenation of biofuel synthesis using metal oxide supported catalysts. Xian I Loo, Chyun Onju, Ching Juan Wei. 2017.
- [57]. Upgrading of bio fuels by the catalytic deoxygenation of biodiesel, Korean Journal of Chemical Engineering, Vol 29. Chong Hyun Ko, Sung Hoon Park, Jong Ki Jean, Kwang Eun Jeong. 2012.
- [58]. Selective deoxygenation of bio mass derived bio-oils within hydrogen modest environment. Kyle. A Rogers, Prof Ying Zheng. 2017.
- [59]. Deoxygenation of triolein to green diesel in an H2 free condition: Effects of transition metal oxide supported on Zeolite. Choo Min Yee, O Lee Ing, Linh Tao Chuan, Lin Yo Chuan. 2009.
- [60]. Alternate energy sources, green chemistry and engineering, Mukesh Doble, Anil 2007.



- [61]. Prospects of biodiesel feedstock as an effective ecofuel source and their challenges, *Advances in ecofuels for a sustainable environment*, E.F Aransiola, B.O Solomon. 2011.
- [62]. Application of transesterification technologies, bioenergy with carbon capture and storage (BECCS), Clean energy for sustainable development, M.A Quander, S.Ahmed. 2017.
- [63]. Advances in bio-oil extraction from non edible seeds and algae biomass, advances in eco fuels for sustainable environment G.Basker, I Abumaebenezer, Selva Kumari. 2019.
- [64]. Lignocellulose based chemical products, bioenergy research, advances and applications. E.D de Jung, Richard j.A Gosselink. 2014.
- [65]. Heterogeneous and homogeneous for petroleum catalysis, Wayne P.Schamuel, Anja Rumpelcker, Joel M. Cizron, Eric C. Scher, Fabio Zuricher. 2016.
- [66]. 13th International symposium of process systems engineering (PSE) 2010. Hye Ji Lee, Jin Min Lee, Computer Aided Chemical Engineering.2018.
- [67]. Ingeniería de Las reacciones Químicas. Tipo de reactores, chemical process engineering Design. By Harry Silla. 2019.
- [68]. Replacing Fossil Fuels and Nuclear Power with Renewable Energy: Utopia or Valid Option? A Swiss Case Study of Bioenergy
- [69]. Raphael Haymoz Renato Lemm Oliver Thees Apr 2020
- [70]. Alternate energy sources, green chemistry and engineering, Mukesh Doble, Anil Kumar. 2007.
- [71]. Prospects of biodiesel feedstock as an effective ecofuel source and their challenges, *Advances in ecofuels for a sustainable environment*, E.F Aransiola, B.O Solomon. 2016.
- [72]. Application of transesterification technologies, bioenergy with carbon capture and storage (BECCS), Clean energy for sustainable development, M.A Quander, S.Ahmed. 2017.
- [73]. Advances in bio-oil extraction from non edible seeds and algae biomass, advances in eco fuels for sustainable environment G.Basker, I Abumaebenezer, Selva Kumari. 2020.
- [74]. Lignocellulose based chemical products, bioenergy research, advances and applications. E.D de Jung, Richard j.A Gosselink. 2014.
- [75]. Heterogeneous and homogeneous for petroleum catalysis, Wayne P.Schamuel, Anja Rumpelcker, Joel M. Cizron, Eric C. Scher, Fabio Zuricher.74), 13th International symposium of process systems engineering (PSE) 2010. Hye Ji Lee, Jin Min Lee,
- [76]. Keskin A, Guru M, Altiparmak D, Aydin K. Using of cotton oil soap stock biodiesel–diesel fuel blends as an alternative diesel fuel. *Renew Energy* 2008;33:553–557. 2008.
- [77]. Canakci M, Van Gerpen J. Biodiesel production from oils and fats with high free fatty acids. *Trans ASAE* 2001;44:1429–36.
- [78]. Papadopoulos CE, Lazaridou A, Koutsoumba A, Kokkinos N, Christoforidis A, Nikolaou N. Optimization of cotton seed biodiesel quality (critical properties) through modification of its fame composition by highly selective homogeneous hydrogenation. *Biores Technol* 2010;101:1812–1819.
- [79]. Srivastava A, Prasad R. Triglycerides-Based Diesel Fuels. *Renew Sust Energy Rev* 2000;4:111–133.
- [80]. Rao P, Gopalakrishnan K. Vegetable Oils and Their Methylesters as Fuels for Diesel Engines. *Indian J Technol* 1991;29:292–29.
- [81]. Aksoy F, Bayrakceken H, Eryilmaz T, Aksoy L. Analyzing the impact of using different methyl esters in a diesel engine on engine performance and emissions. *Energy Educ Sci Technol Part A* 2011;27:25–34.
- [82]. Aksoy F. The effects of sunflower oil and soybean oil – diesel fuel blends on engine performance and emissions. *Energy Educ Sci Technol Part A* 2011;27:419–426.
- [83]. Aksoy F, Bayrakceken H, Baydır SA, Yavuz H. The effects on the engine performance and emission of pre-heating application in the canola oil methyl ester. *Electronic J Vehicle Technol* 2009;1:25–33 [in Turkish].
- [84]. Altun S. Fuel properties of biodiesels produced from different feedstocks. *Energy Educ Sci Technol Part A* 2011;26:165–174.
- [85]. Fukuda H, Kondo A, Noda H. Biodiesel Fuel Production by Transesterification of Oils. *J Biosci Bioeng* 2001;92:405–416.
- [86]. Tyson K, S. Biodiesel Handling and Use Guidelines, Report of National Renewable Energy Laboratory, NREL/TP-580-3004, USA, 1–3, 2001.
- [87]. Van Gerpen J. Biodiesel processing and production, *Fuel Procg Technol* 2005;86:1097–1107.
- [88]. Cetinkaya M, Ulusoy Y, Tekin Y, Karaosmanoglu F. Engine and winter road test performances of used cooking oil originated biodiesel. *Energy Convers Manage* 2005;46:1279–1291.
- [89]. Arkoudeas P, Kalligeros S, Zannikos G, Anastopoulos G, Karonis D, Korres D. Lois,E. Study of using JP-8 aviation fuel and biodiesel in CI engines. *Energy Convers Manage* 2002;44:1013–1025.
- [90]. Altin R, Cetinkaya S, Yucesu HS. The potential of using vegetable oil fuels as fuel for diesel engines. *Energy Convers Manage* 2001;42:529–38.
- [91]. Dorado MP, Ballesteros E, Arnal JM, Gomez J, Gimenez Lopez FJ. Exhaust emissions from a diesel engine fueled with transesterified waste olive oil. *Fuel* 2003;82:1311–1315.
- [92]. Nwafor OMI. Emission characteristics of diesel engine operating on rapeseed methyl ester. *Renew Energy* 2004;29:119–129.
- [93]. Usta N. An experimental study on performance and exhaust emissions of a diesel engine fuelled with tobacco seed oil methyl ester. *Energy Conversion Management* 2005;46:2373–2386.
- [94]. Monyem A, Van Gerpen JH. The effect of biodiesel oxidation on engine performance and emissions. *Biomass Bioenergy* 2001;20:317–32.
- [95]. Usta N, Ozturk E, Can O, Conkur ES, Nas S, Con AH, Can AC, Topcu M. Combustion of biodiesel fuel produced from hazelnut soapstock/waste sunflower oil mixture in a diesel engine. *Energy Convers Manage* 2005;46:741–755.
- [96]. Scholl KW, Sorenson SC. Combustion of Soybean Oil Methyl Ester in a Direct Injection Diesel Engine, SAE Paper, No.930934, 1999.
- [97]. Catalysis, Green Chemistry and Sustainable Energy. Antonio Zarli in studies in surface science and catalysis 2020.
- [98]. 22nd European Symposium on Computer Aided Process Engineering. Binta Z. Bello, Meshang Wang in Computer Aided Chemical Engineering 2012.
- [99]. Catalysis, Green Chemistry and Sustainable Energy. Antonio Zarli in the Studies of Surface Science and Catalysis 2020.
- [100]. Anaerobic biovalorization of leather industry solid waste and production of high Biovalorization of wastes in renewable chemicals and biofuels. Value added biomolecules and biofuels. Ramani Kondasony, Sekarm Ganesen, 2020.
- [101]. Using Microwave radiation and ZrO as a catalyst for the complete conversion of oils, cooking oils and

- Microalgae to biodiesel. Miri Koberg, Aharon Godaken in New and Future development in Catalysis 2013.
- [102]. Carbons and Graphites: Surface properties of P.M.A Sherwood in Encyclopedia of Materials. Science and Technology 2001.
- [103]. Importance of Physicochemical characterization of Nanoparticles in Pharmaceutical product development.
- [104]. Nidhi Raval, Rakesh K. Tekede in Basic Fundamentals of Drug Delivery. 2019.
- [105]. Development of Stable Oxygen Carrier Materials for Chemical Looping Processes—A Review, Yoran De Vos, Marijke Jacobs, Pascal Van De Vort July 2020.
- [106]. Hydrogenation for biofuel production. Prof. Derek Creaser, Hu Chaoquan. 2012.
- [107]. Development and characterization of heterogeneous kaolin/ash based catalyst system, Edeh Friday, J.m Joel, Jibrin M Yelwa, J.M Joel, Jeffery Barminas. Dec 2018.
- [108]. Synthetic methods 1- chiral pool and diastereoselective methods. comprehensive Chirality Y Guindon. 2012.
- [109]. Synthetic methods iii-catalytic Methods C-C bond formation. S.Koboyashi, Y. Yamashida (2012).
- [110]. Hydrotreating lipids for aviation biofuels derived from extraction of wet asnd dry algae by Ze Shi Bing, Wei Zhao Shun. 2008.
- [111]. Direct hydrogenation of amides to alcohols and amines under mild conditions. Ekambaram Balaraman, Boopathy Gnanapra Kajam, Linda J. W Shimon, David Milstein. Nov 4 2010.
- [112]. Hydrogenation for biofuel production. Prof. Derek Creaser, Hu Chaoquan. 2012.
- [113]. Overview on catalytic deoxygenation of biofuel synthesis using metal oxide supported catalysts. Xian I Loo, Chyun Onju, Ching Juan Wei. 2017.
- [114]. Upgrading of bio fuels by the catalytic deoxygenation of biodiesel, Korean Journal of 11Chemical Engineering, Vol 29. Chong Hyun Ko, Sung Hoon Park, Jong Ki Jean, Kwang Eun Jeong. 2011.
- [115]. Selective deoxygenation of bio mass derived bio-oils within hydrogen modest environment. Kyle. A Rogers, Prof Ying Zheng. 2017.
- [116]. Deoxygenation of triolein to green diesel in an H<sub>2</sub> free condition: Effects of transition metal oxide supported on Zeolite. Choo Min Yee, O Lee Ing, Linh Tao Chuan, Lin Yo Chuan. 2020.
- [117]. Alternate energy sources, green chemistry and engineering, Mukesh Duble, Anil2007.
- [118]. Prospects of biodiesel feedstock as an effective ecofuel source and their challenges, Advances in ecofuels for a sustainable environment , E.F Aransiola, B.O Solomon. 2012.
- [119]. Application of transesterification technologies, bioenergy with carbon capture and storage (BECCS), Clean energy for sustainable development, M.A Quander, S.Ahmed. 2017.
- [120]. Advances in bio-oil extraction from non edible seeds and algae biomass, advances in eco fuels for sustainable environment G.Basker, I Abumaebenezer, Selva Kumari. 2012.
- [121]. Lignocellulose based chemical products, bioenergy research, advances and applications. E.D de Jung, Richard j.A Gosselink. 2014.
- [122]. Heterogeneous and homogeneous for petroleum catalysis, Wayne P.Schamuel, Anja Rumpelcker, Joel M. Cizron, Eric C. Scher, Fabio Zuricher. 2017.
- [123]. 13th International symposium of process systems engineering (PSE) 2010. Hye Ji Lee, Jin Min Lee, Computer Aided Chemical Engineering.2018.
- [124]. Ingenieria de Las reacciones Quimicas. Tipo de reactores, chemiocol process engineering Design. By Harry Silla. 2019.
- [125]. Replacing Fossil Fuels and Nuclear Power with Renewable Energy: Utopia or Valid Option? A Swiss Case Study of BioenergyRaphael Haymoz Renato Lemm Oliver Thees Apr 2020
- [126]. Alternate energy sources, green chemistry and engineering, Mukesh Duble, Anil Kumar. 2007.
- [127]. Prospects of biodiesel feedstock as an effective ecofuel source and their challenges, Advances in ecofuels for a sustainable environment , E.F Aransiola, B.O Solomon. 2012.
- [128]. Application of transesterification technologies, bioenergy with carbon capture and storage (BECCS), Clean energy for sustainable development, M.A Quander, S.Ahmed. 2017.
- [129]. Advances in bio-oil extraction from non edible seeds and algae biomass, advances in eco fuels for sustainable environment G.Basker, I Abumaebenezer, Selva Kumari. 2014.
- [130]. Lignocellulose based chemical products, bioenergy research, advances and applications. E.D de Jung, Richard j.A Gosselink. 2014.
- [131]. Heterogeneous and homogeneous for petroleum catalysis, Wayne P.Schamuel, Anja Rumpelcker, Joel M. Cizron, Eric C. Scher, Fabio Zuricher. 2013.
- [132]. 13th International symposium of process systems engineering (PSE) 2010. Hye Ji Lee, Jin Min Lee, Computer Aided Chemical Engineering.2018.
- [133]. Demirbas A. Progress and recent trends in biofuels. Prog Energy Combust Sci 2007;33:1–18. 2011.
- [134]. Keskin A, Guru M, Altiparmak D, Aydin K. Using of cotton oil soap stock biodiesel–diesel fuel blends as an alternative diesel fuel. Renew Energy 2008;33:553–557. 2012.
- [135]. Canakci M, Van Gerpen J. Biodiesel production from oils and fats with high free fatty acids. Trans ASAE 2001;44:1429–36. 2016.
- [136]. Papadopoulos CE, Lazaridou A, Koutsoumba A, Kokkinos N, Christoforidis A, Nikolaou N. Optimization of cotton seed biodiesel quality (critical properties) through modification of its fame composition by highly selective homogeneous hydrogenation. Biores Technol 2010;101:1812–1819.
- [137]. Srivastava A, Prasad R. Triglycerides-Based Diesel Fuels. Renew Sust Energy Rev 2000;4:111–133.
- [138]. Rao P, Gopalakrishnan K. Vegetable Oils and Their Methyl esters as Fuels for Diesel Engines. Indian J Technol 1991;29:292–29.
- [139]. Aksoy F, Bayrakceken H, Eryilmaz T, Aksoy L. Analyzing the impact of using different methyl esters in a diesel engine on engine performance and emissions. Energy Educ Sci Technol Part A 2011;27:25–34.
- [140]. Aksoy F. The effects of sunflower oil and soybean oil – diesel fuel blends on engine performance and emissions. Energy Educ Sci Technol Part A 2011;27:419–426.
- [141]. Aksoy F, Bayrakceken H, Baydır SA, Yavuz H. The effects on the engine performance and emission of pre-heating application in the canola oil methyl ester. Electronic J Vehicle Technol 2009;1:25–33 [in Turkish].
- [142]. Altun S. Fuel properties of biodiesels produced from different feedstocks. Energy Educ Sci Technol Part A 2011;26:165–174.
- [143]. Fukuda H, Kondo A, Noda H. Biodiesel Fuel Production by Transesterification of Oils. J Biosci Bioeng 2001;92:405–416.
- [144]. Tyson K, S. Biodiesel Handling and Use Guidelines, Report of National Renewable Energy Laboratory, NREL/TP-580-3004, USA, 1–3, 2001.
- [145]. Van Gerpen J. Biodiesel processing and production, Fuel Progc Technol 2005;86:1097–1107.



- [146]. Cetinkaya M, Ulusoy Y, Tekin Y, Karaosmanoglu F. Engine and winter road test performances of used cooking oil originated biodiesel. *Energy Convers Manage* 2005;46:1279–1291.
- [147]. Arkoudeas P, Kalligeros S, Zannikos G, Anastopoulos G, Karonis D, Korres D. Lois, E. Study of using JP-8 aviation fuel and biodiesel in CI engines. *Energy Convers Manage* 2002;44:1013–1025.
- [148]. Altin R, Cetinkaya S, Yucsu HS. The potential of using vegetable oil fuels as fuel for diesel engines. *Energy Convers Manage* 2001;42:529–38.
- [149]. Dorado MP, Ballesteros E, Arnal JM, Gomez J, Gimenez Lopez FJ. Exhaust emissions from a diesel engine fueled with transesterified waste olive oil. *Fuel* 2003;82:1311–1315.
- [150]. Nwafor OMI. Emission characteristics of diesel engine operating on rapeseed methyl ester. *Renew Energy* 2004;29:119–129.
- [151]. Usta N. An experimental study on performance and exhaust emissions of a diesel engine fuelled with tobacco seed oil methyl ester. *Energy Conversion Management* 2005;46:2373–2386.
- [152]. Monyem A, Van Gerpen JH. The effect of biodiesel oxidation on engine performance and emissions. *Biomass Bioenergy* 2001;20:317–32.
- [153]. Usta N, Ozturk E, Can O, Conkur ES, Nas S, Con AH, Can AC, Topcu M. Combustion of biodiesel fuel produced from hazelnut soapstock/waste sunflower oil mixture in a diesel engine. *Energy Convers Manage* 2005;46:741–755.
- [154]. Scholl KW, Sorenson SC. Combustion of Soybean Oil Methyl Ester in a Direct Injection Diesel Engine, SAE Paper, No.930934, 1999.
- [155]. Catalysis, Green Chemistry and Sustainable Energy. Antonio Zarli in studies in surface science and catalysis 2020.
- [156]. 22nd European Symposium on Computer Aided Process Engineering. Binta Z. Bello, Meshang Wang in Computer Aided Chemical Engineering 2012.
- [157]. Ingeniería de Las reacciones químicas. tipo de reactores, chemical process engineering design. By Harry Silla. 2012.
- [158]. Effect of the SiO<sub>2</sub> support on the catalytic performance of Ag/ZrO<sub>2</sub>/SiO<sub>2</sub> catalysts for the single-bed production of butadiene from ethanol. Vanessa Lebarbier, Daggle Mathew, Robert A Daggle. 2018.
- [159]. Selective synthesis of butadiene directly from aqueous ethanol over high performance multifunctional catalyst based on ZnZrSi oxide system. Na Liu, LinZhang, Kangzhou Wang, Lishu Shao, 2022.
- [160]. Synthesis of cyclic carbonates of different epoxides using CO<sub>2</sub> as a C1 building block over Ag/TUD-1 mesoporous silica catalyst: A solvent free approach. Saura Keshri, Sudip Bhatta, Charjee. Anirud, 2022.
- [161]. 158), Selective direct conversion of aqueous ethanol into butadiene via rational design of multifunctional catalysts. Kangzhou Wang, Xiabo Peng, Xiaoyu Guo 2021.
- [162]. Metal support interactions in CeO<sub>2</sub> and SiO<sub>2</sub> supported Cobalt catalysts. Effect of support morphology and reducibility and interfacial configuration. Zhangai Liu, Junhao Li, Michael Buettner 2019.
- [163]. Impact of Biodiesel combustion on NO<sub>x</sub> emissions and their reduced approaches. S.M Palash, M.A Kalam, H.H Masjuli 2013.
- [164]. Life cycle assessment of hydrogenated biodiesel production from waste cooking oil using the catalytic cracking and hydrogenation method. Junya Yeno, Tatsu Kia, Kasuu Nakamura, Kazoo Yamuda 2015.
- [165]. Upgrading Biodiesel from Vegetable Oils by Hydrogen Transfer to its Fatty Esters Zhiyao Lu, Valeriy Cherepakhin, Talya Kapenstein, Travis J. Williams 2015.
- [166]. Taguchi method for investigating performance parameters and energy of a diesel engine using four types of diesel fuel. Dara Khalid, Soorkeu A, Atroochi. 2016.
- [167]. <https://www.sciencedirect.com/science/article/abs/pii/S2468823118301986>.
- [168]. <https://www.sciencedirect.com/topics/engineering/hydrodeoxygenation>.
- [169]. [www.hindawi.com/room/temperature/synthesis](http://www.hindawi.com/room/temperature/synthesis)
- [170]. [https://www.researchgate.net/figure/Simplified-flow-chart-of-biodiesel-production-through-transesterification-22\\_fig2\\_348002192](https://www.researchgate.net/figure/Simplified-flow-chart-of-biodiesel-production-through-transesterification-22_fig2_348002192)
- [171]. <https://www.physicsclassroom.com/class/thermalP/Lesson-2/Calorimeters-and-Calorimetry>
- [172]. [https://www.mdpi.com/catalysts/catalysts-10-00926/article\\_deploy/html/images/catalysts-10-00926-g016.png](https://www.mdpi.com/catalysts/catalysts-10-00926/article_deploy/html/images/catalysts-10-00926-g016.png)
- [173]. [https://www.researchgate.net/figure/Flowchart-for-the-transesterification-and-hydrogenation-process\\_fig1\\_335385248](https://www.researchgate.net/figure/Flowchart-for-the-transesterification-and-hydrogenation-process_fig1_335385248)
- [174]. <https://www.sciencedirect.com/science/article/abs/pii/S2468823118301986>
- [175]. <https://www.sciencedirect.com/topics/engineering/hydrodeoxygenation>.
- [176]. [https://www.researchgate.net/figure/Hydrodeoxygenation-HDO-process-for-the-reaction-pathway-producing-pyrolytic-products\\_fig4\\_277944991](https://www.researchgate.net/figure/Hydrodeoxygenation-HDO-process-for-the-reaction-pathway-producing-pyrolytic-products_fig4_277944991)